Ultrafast Nonlinear X-ray Spectroscopy of Molecules: Theoretical Challenges.

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A systematic description of coherent ultrafast X-ray spectroscopies in terms of nonlinear response functions (NRF) and susceptibilities is presented. This approach, which proved very useful in modeling optical measurements, is extended to the X-ray regime. The NRF are expressed as sums of *Liouville-space pathways*, which provide an intuitive picture for the time evolution of the electronic and nuclear degrees of freedom. NRF also disentangle the roles of the pulses and the molecular response. Correlation function expressions of charge and current densities provide a unified treatment and classification of information content of the various techniques and connect them with their optical counterparts. Both pure x-ray and joint optical/x-ray techniques including pump probe, x-ray fluorescence, four wave mixing, coherent Raman time resolved EXAFS and diffraction measurements will be discussed. Such multidimensional x-ray spectroscopies could provide a wealth of novel structural and dynamical information. The relative and the transnational motions of electron-hole pairs in conjugated molecules and nanostructures are clearly separated in real space and may be directly probed using x-ray signals which provide a localized (atom-specific) probes of core excitations in molecules. Other possible applications include chromophore (e.g.. Porphyrin) aggregates, and reactive systems.

S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Oxford, New York, 1995.

"Multidimensional Femtosecond Correlation Spectroscopies of Electronic and Vibrational Excitations," S. Mukamel, *Ann. Rev. Phys. Chem.* **51**, 691-729 (2000).

"Time-Resolved X-Ray Spectroscopies; Nonlinear Response Functions and Liouville-Space Pathways," S. Tanaka, V. Chernyak and S. Mukamel, *Phys. Rev. A*, **63**, 063405 (2001).

"Simulation of Frequency and Wavevector resolved femtosecond resonant x-ray emission of molecular chains," S. Tanaka and S. Mukamel, *Phys. Rev. A.*, **64**, 032503/1-13, (2001).

"X-Ray Four-Wave Mixing in Molecules," S. Tanaka and S. Mukamel, *J. Chem. Phys.* **116***,* 1877-1891 (2001).